Modifications in the Catalytic Properties of Nickel Supported on Different Dielectric Oxides

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The hydrogenation of 1-butene and 1,3-butadiene has been carried out over a series of dielectric-oxide-supported nickel catalysts at temperatures ranging from 60 to 120 °C and atmospheric pressure. The catalytic activity and selectivity of these systems were found to be extremely sensitive to the nature of the support medium, the hydrogen content of the reactant gas mixture, and the reaction temperature. High-resolution transmission electron microscopy examinations provided evidence that the active state of the catalyst was associated with the partial reduction of the support, particularly in the vicinity of the dispersed metal phase. With some of the dielectric oxides it was essential for the system to remain on stream for prolonged periods of time to achieve the optimum activity. It is proposed that the induction period is related to the time required to reduce the support to a lower oxide state, which is capable of inducing electronic perturbations in the dispersed metal particles. It is suggested that the initial role of the metal in this interaction is to function as a dissociation center for hydrogen, thus providing a source of atomic species for the subsequent partial reduction of the support. It was significant to find that when nickel was supported on γ-alumina, an oxide that does not undergo this type of transformation, the catalytic performance for the respective hydrogenation reactions under these conditions was extremely poor.

Introduction

Traditional supported metal catalysts depend to a large degree upon the nature of the interaction between the two components, and as a consequence, this is the key factor to be considered if the intention is to induce changes in the performance of the system. Clearly, substantial benefits would be derived if one could accurately fine-tune the strength of the interaction by careful choice of the support. In this respect, use of certain ferroelectric materials as support media may offer a means of controlling the catalytic properties of dispersed metal particles. It is well-established that the materials that belong to this class undergo phase transitions at their respective Curie temperatures, and under such conditions substantial changes in the relative permittivity are generally observed.[1−4] If one could effectively channel these transformations in electrical properties with respect to modification of the behavior of a supported metal particle, the resultant catalytic activity of the system might be dramatically enhanced. One further option to exploit such perturbations in electronic properties would be to disperse a given metal on a series of materials and correlate the catalytic performance of each system with the respective relative dielectric constants of the support medium.

In the past, the physical properties of ceramic materials have been taken advantage of only in catalytic oxidation and photocatalytic processes. Perovskite type ceramic oxides are predominately utilized as oxidation catalysts since the mobility of oxygen species on the surface and their activation in the bulk are readily influenced by the choice of cations in the ABO_3 structure.[5−7] The use of ceramics and ferroelectric materials in heterogeneous catalysis is an area that has received limited attention despite the early work by Parravano [8] who demonstrated that significant changes could be induced in the performance of an impregnated metal at specific temperatures. These changes in activity were correlated to phase transitions occurring within the support materials, potassium and sodium niobates. The photocatalytic properties of similar perovskite type ceramic oxides, in particular $SrTiO_3$, have been shown to be strongly dependent upon the method of preparation.[9,10] This oxide has been employed in the study of the generation of hydrogen and oxygen from the decomposition of water:[11,12] a reaction that has been shown

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to take place at a zero applied potential.[13] The uses of photocatalytic processes are key factors in the conversion of solar energy, an area of extreme importance in these times of increasing environmental awareness. Although these ceramic materials have been used in such a diverse range of reactions, very little is known about their potential as catalyst support media for more demanding hydrocarbon conversion reactions.

In a previous investigation, we demonstrated that when nickel was supported on ceramic and ferroelectric materials possessing a wide variation in dielectric constants, optimization in the catalytic activity of the metal toward hydrogenation of ethylene could be achieved at characteristic temperatures for each support.[14] For example, the Ni/BaTiO$_3$ catalyst system exhibited a sharp maximum for the conversion of ethylene at 120 °C, a temperature where the oxide is known to undergo a phase transition from a tetragonal to a cubic structure[1,4] and where the value of the permittivity reached a maximum. It was suggested that the changes in the strength of the metal−support interaction and electronic perturbations caused by the structural transition in BaTiO$_3$ exerted a strong influence on the nickel particles that was reflected by a massive change in the catalytic behavior.

The objective of the current study is to determine the impact of a series of different oxide supports on the catalytic performance of nickel particles under more demanding hydrogenation conditions. The introduction of reactants that offer a choice of reaction pathways will enable one to elucidate the nature of the perturbations in the catalytic activity and permit correlations to be made with the changes occurring in the support material. For this purpose, we have elected to study the hydrogenation of 1-butene and 1,3-butadiene, respectively, under various reaction conditions.

Experimental Section

Materials. The preparation of the 5 wt % supported nickel catalysts was carried out by using a standard incipient wetness technique, which has been described in detail in a previous paper.[15] Each support medium was impregnated with an aqueous solution of nickel nitrate, which contained the appropriate amount of salt necessary to achieve the desired metal loading. The catalyst precursor was first calcined in air at 250 °C for 4 h to convert the metal nitrate to the oxide state. The calcined catalyst was then flushed in helium at room temperature before being reduced at 350 °C in a 10% H$_2$/He mixture for 24 h. The reduced catalyst was cooled in helium and passivated at ambient temperature in a 2% O$_2$/He mixture for 1 h before being removed from the reactor and stored for future use. For comparison purposes, a selected number of experiments were carried out with a corresponding set of 5 wt % supported silver catalysts, which were prepared by a similar procedure to that described above.

The gases used in this work, helium (99.999%), hydrogen (99.999%), carbon monoxide (99.99%), 1-butene (99.95%), and 1,3-butadiene (99.95%), were obtained from Medical Technical Gases and used without any further purification. Reagent grade nickel nitrate [Ni(NO$_3$)$_2$·6H$_2$O], silver nitrate [AgNO$_3$], used in the catalyst preparation, and TiO$_2$ were obtained from

Fisher Scientific. The γ-Al$_2$O$_3$ was supplied by the Degussa Corporation, Ta$_2$O$_5$ was obtained from Alfa Aesar, and BaTiO$_3$ and CaTiO$_3$ were supplied by Rhone-Poulenc, and all oxide powders were used in the "as-received" condition.

Apparatus and Procedures. The apparatus used throughout this study consisted essentially of a quartz flow reactor tube (2.5-cm i.d. and 40 cm long). The tube was fitted with a quartz frit located approximately in the middle of the reactor, which was heated by a split vertical tube furnace. The gas flow to the reactor was precisely regulated by the use of MKS mass flow controllers allowing a constant composition of a desired reactant feed to be delivered to the catalyst system. Catalyst samples (100 mg) were placed on the quartz frit, and the tube was aligned in such a manner that the frit was always in approximately the same position in the reactor. After reduction in a 10% H$_2$/He mixture for 2 h at 350 °C, the temperature was lowered to the desired level in the same mixture. Once the set reaction temperature was attained, the predetermined hydrocarbon/H$_2$/He reactant mixture was introduced to the reduced catalyst sample at a flow rate of 120 mL min^{-1}, until a steady-state conversion was realized. Hydrogenation reactions were carried out at temperatures ranging from 60 to 120 °C and atmospheric pressure for periods of up to 24 h. The reaction was followed as a function of time by sampling the inlet and outlet gas streams at regular intervals. The reactants and products were analyzed by gas chromatography by using a 30 m megabore (GC-AL) capillary column in a Varian 3400 G.C. unit.

The nature and characteristics of all the catalyst support materials were established by using a combination of techniques, including high-resolution transmission electron microscopy (HRTEM), temperature-programmed oxidation/reduction (TPO/TPR), X-ray diffraction (XRD), and nitrogen BET surface area measurements. The results of characterization studies carried out on the fresh supported nickel catalysts were reported in a previous paper.[14]

The nickel and silver catalysts were examined after use to establish the existence of any changes in either the support structure or the morphology of the metal particles that may have occurred during the hydrocarbon hydrogenation reactions. To obtain meaningful information on these aspects, it was essential to passivate the samples in a 2% O$_2$/Ar stream at room temperature prior to removal from the reactor. Failure to perform this step resulted in complete oxidation of the metal particles when the specimen was taken out of the reducing environment and exposed directly to air, thus giving an incorrect analysis of the chemical state and a false impression of the morphological characteristics of the catalyst.

HRTEM studies were performed in a JEOL 2000EX II electron microscope fitted with a high-resolution pole piece capable of giving a lattice resolution of 0.18 nm. Suitable transmission specimens were prepared by the ultrasonic dispersion of catalyst samples in isobutanol and then the addition of a drop of the resultant suspension to a holey carbon support grid. Powder XRD patterns of the used catalysts were obtained with a Scintag diffractometer by using nickel-filtered Cu Kα radiation. Diffraction patterns were recorded over a range of 2θ angles from 10 to 90° and compared with the known X-ray powder files to establish the phase identities. These patterns were compared with those of the fresh catalyst samples.

Results

1. Flow Reactor Studies. To evaluate the performance of the oxide-supported nickel catalysts for the hydrogenation of 1-butene and 1,3-butadiene, experiments were carried out for extended periods of time with various hydrocarbon/hydrogen mixtures at temperatures ranging from 60 to 120 °C. A detailed explanation and the definitions used to calculate the selectivities and product ratios associated with these hydrogenation reactions are given in Tables 1 and 4. Blank experi-

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Table 1. Comparison of the Behavior of Various Oxide-Supported 5 wt % Nickel Catalysts for the Hydrogenation of 1-Butene (C_4H_8/H_2 = 1:1) at 120 °C

support medium	induction period (min)	% conversion	*trans/ cis*-2-butene	S_1^a
$BaTiO_3$	1450	56.18	0.52	0.30
Ta_2O_5	20	67.68	0.49	0.28
TiO_2	50	59.32	0.23	0.17
$CaTiO_3$	150	83.65	0.97	0.32
Al_2O_3		2.11		0.11

^{a} S_1 = (*trans*-2-butene + *cis*-2-butene)/(*trans*-2-butene + *cis*-2-butene + butane).

ments were conducted under the same conditions with the respective pristine support materials. No evidence for hydrocarbon conversion was observed in these latter systems.

1.1. Catalytic Hydrogenation and Isomerization of 1-Butene by Supported Nickel. The results presented in Table 1 show the total conversion of 1-butene, in the presence of an equal amount of hydrogen at 120 °C, and product selectivities obtained at steady-state conditions for the five oxide-supported nickel catalysts. Inspection of these data reveals that the catalytic activity, as measured by 1-butene conversion, and selectivity of nickel exhibits a wide variation depending upon the nature of the oxide support. It is apparent that while substantial hydrocarbon conversion levels were attained with all the dielectric-supported metal systems, the catalytic activity of the γ-alumina-supported nickel catalyst was very low and did not increase with longer reaction time. Examination of these results also shows the existence of significant differences in the selectivity patterns toward products of isomerization reactions (S_1). It is interesting to find that in this regard, Ni/CaTiO$_3$ and Ni/BaTiO$_3$ displayed similar behavior despite the fact that the two systems exhibited different levels of catalytic activity. In all cases, however, as one would expect under these conditions, the complete hydrogenation of 1-butene to butane was the favored reaction step over the isomerization reaction.

Another aspect to emerge from this set of experiments was the finding of dramatic differences in the length of the induction period required to achieve the optimum activity with the various systems. When the metal particles were supported on CaTiO$_3$, and particularly BaTiO$_3$, extensive periods of time were required to attain measurable catalytic activity. An example of this behavior is presented for the Ni/BaTiO$_3$—1-butene/hydrogen (1:1) system in Figure 1, where it can be seen that an induction period of almost 24 h was required for the catalyst to perform to its full potential.

In another series of experiments, the effect of varying the reaction temperature, on the activity and selectivity of a 5 wt % Ni/TiO$_2$ catalyst for the hydrogenation and isomerization of 1-butene, was investigated and the results are given in Table 2. It is apparent that as the reaction temperature was progressively raised from 60 to 120 °C, there was a corresponding decrease in the time required to reach the highest level of catalytic activity. It was also intriguing to find that the percent conversion did not show a steady increase with temperature but instead exhibited a maximum value at about 90 °C. A further interesting feature of these experiments was that although significant changes were

Figure 1. Percent product distribution as a function of time for the Ni/BaTiO$_3$-catalyzed hydrogenation of 1-butene at 120 °C.

Table 2. Comparison of the Behavior of a 5 wt % Ni/TiO$_2$ Catalyst for the Hydrogenation of 1-Butene (C_4H_8/H_2 = 1:1) at Different Temperatures

temp (°C)	induction period (min)	% conversion	*trans/ cis*-2-butene	S_1
60	6200	74.13	0.56	0.17
90	1021	92.14	1.11	0.15
120	50	59.32	0.23	0.17

Table 3. Comparison of the Behavior of a 5 wt % Ni/CaTiO$_3$ Catalyst as Function of the 1-Butene/Hydrogen Ratio at 120 °C

C_4H_8/H_2	induction period (min)	% conversion	*trans/ cis*-2-butene	S_1
1.5	1250	64.93	0.38	0.29
1	560	71.07	0.5	0.32
0.92	160	46.21		0.12
0.79	845	93.49	1.28	0.18
0.67	1105	4.86		0.12
0.5	1876	4.11		0.14

observed in the *trans*-2-butene/*cis*-2-butene ratio as a function of temperature, there was no equivalent change in the overall selectivity, S_1, indicating that the formation of *n*-butane dominated these reactions.
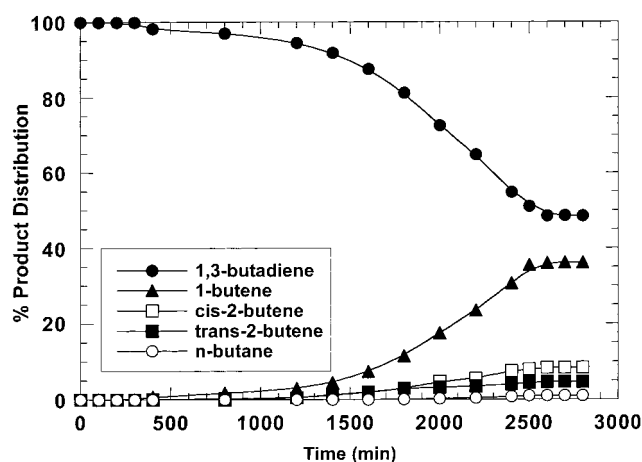
One can furnish a reasonable argument based on the notion that if the induction period is directly related to a transformation in the chemical state of the support medium, then the amount of hydrogen present in the feed might also be expected to exert an impact on this phenomenon. In an attempt to gain a clearer insight into the factors that control the intrinsic activity of these dielectric-supported metal systems the influence of hydrogen was investigated. Since the 5 wt % Ni/CaTiO$_3$ sample exhibited the highest activity and displayed a relatively short induction period, this system was chosen to study the effect of varying the hydrocarbon/hydrogen feed ratio on the catalyst performance.

Table 3 details the changes in behavior of the Ni/CaTiO$_3$ system that occurred when the 1-butene/hydrogen ratio was varied in a systematic fashion from 1.5 to 0.5, while a constant temperature of 120 °C was maintained. It can be seen that as the hydrogen content of the reactant was raised, the induction period associated with this reaction was found to decrease to a minimum, at a ratio of 0.92, before exhibiting an increase at higher C_4H_8/H_2 ratios. Other trends that are apparent from this sequence of reactions include the

Table 4. Comparison of the Behavior of Various Oxide-Supported 5 wt % Nickel Catalysts for the Hydrogenation of 1,3-Butadiene (C_4H_6/H_2 = 1:1) at 120 °C

support media	induction period (min)	% conversion	*trans*/*cis*-2-butene	$S_2{}^a$	$B_1/B_2{}^b$
BaTiO$_3$	2600	51.08	0.59	0.97	2.51
Ta$_2$O$_5$	20	51.11	0.86	0.79	2.13
TiO$_2$	0	69.65	0.28	0.97	4.28
CaTiO$_3$	30	73.99	0.37	0.92	2.58
Al$_2$O$_3$	0	0.30	0.17	0.52	1.46

^{a} S_2 = (1-butene + *trans*-2-butene + *cis*-2-butene)/(1-butene + *trans*-2-butene + *cis*-2-butene + butane). ^{b} B_1/B_2 = (1-butene)/(*trans*-2-butene + *cis*-2-butene).

Figure 2. Percent product distribution as a function of time for the Ni/BaTiO$_3$-catalyzed hydrogenation of 1,3-butadiene at 120 °C.

finding of a precipitous decline in the 1-butene conversion as the C_4H_8/H_2 ratio dropped to 0.67, which coincided with the reestablishment of an extensive induction period. The selectivity, S_1, decreased with increasing H$_2$ content, which is an expected tendency as the formation of *n*-butane becomes more dominant under these favorable hydrogenation conditions.

1.2. Catalytic Hydrogenation of 1,3-Butadiene by Supported Nickel. In an attempt to seek more information on the unexpected pattern of behavior observed with the oxide-supported nickel systems, this same set of catalysts was used to investigate a somewhat more complex system, namely, the hydrogenation of 1,3-butadiene. The results presented in Table 4 enable one to compare the performance of nickel dispersed on the five different oxide carriers for the 1,3-butadiene/hydrogen (1:1) reaction at 120 °C. As with the previous hydrogenation system, the activity and selectivity of nickel was highly dependent upon the nature of the support material. The major difference, however, was that, with the exception of Ni/BaTiO$_3$, the time required for each catalyst to attain optimum activity was quite short. In the former case, an induction period of approximately 43 h was necessary to achieve an activity level that was comparable to those of the other dielectric-supported catalysts. The reactivity profile for the Ni/BaTiO$_3$–1,3-butadiene/hydrogen (1:1) system at 120 °C is shown in Figure 2. It was significant to find that once again the nickel/γ-alumina system was virtually inactive under the prevailing reaction conditions.

From Table 4, it is apparent that the performance of the metal varies considerably as a function of the

Table 5. Comparison of the Behavior of a 5 wt % Ni/TiO$_2$ Catalyst for the Hydrogenation of 1,3-Butadiene (C_4H_6/H_2 = 1:1) at Different Temperatures

temp (°C)	induction period (min)	% conversion	*trans*/*cis*-2-butene	S_2	B_1/B_2
60	510	50.30	0.45	1.02	3.65
90	20	60.11	0.34	0.98	4.04
120	0	69.65	0.28	0.97	4.28

Table 6. Comparison of the Behavior of a 5 wt % Ni/CaTiO$_3$ Catalyst as a Function of the 1,3-Butadiene/Hydrogen Ratio at 120 °C

C_4H_6/H_2	induction period (min)	% conversion	*trans*/*cis*-2-butene	S_2	B_1/B_2
1	30	73.99	0.37	0.92	2.58
0.92	65	69.42	0.50	0.78	2.17
0.79	420	47.33	0.83	0.70	1.83
0.67	40	92.41	0.46	0.74	1.98
0.5	20	58.58	1.03	0.41	1.46

support medium, with Ni/CaTiO$_3$ being the most active catalyst for the hydrogenation of 1,3-butadiene at 120 °C. When nickel was supported on either CaTiO$_3$ or BaTiO$_3$, similar selectivity patterns were obtained despite the fact that the former catalyst was considerably more active. In both these systems, 1,3-butadiene preferentially underwent a 1,2 addition to form 1-butene, a partially hydrogenated species. When the metal was supported on TiO$_2$, a similar selectivity, S_2, was achieved along with a higher B_1/B_2 ratio, indicating that in this case, 1,3-butadiene tended to undergo a 1,2 addition rather than a 1,4-addition of hydrogen. The highest *trans*-2-butene/*cis*-2-butene ratio was realized with a 5 wt % Ni/Ta$_2$O$_5$ catalyst where similar amounts of each isomer were formed.

The effect of increasing the reaction temperature from 60 to 120 °C on the catalytic behavior of a Ni/TiO$_2$ catalyst for the hydrogenation of a 1,3-butadiene/hydrogen (1:1) reactant feed is given in Table 5. As with the hydrogenation of but-1-ene, an increase of the reaction temperature led to a reduction in the induction period associated with these supported nickel catalysts. As the temperature was gradually raised, there was a concomitant increase in the overall conversion of 1,3-butadiene and a corresponding decrease in the *trans*-2-butene/*cis*-2-butene ratio. In contrast, the values of S_2 and B_1/B_2 ratios did not appear to exhibit any major changes as a function of reaction temperature.

In a final series of experiments, the effect of altering the hydrocarbon/hydrogen ratio was investigated and for this purpose, we elected to study the behavior of the Ni/CaTiO$_3$ system at 120 °C. Inspection of the data presented in Table 6 shows that the induction period went through a maximum at a C_4H_6/H_2 ratio of 0.79. Once again, the pattern of behavior exhibited by the supported nickel catalyst did not follow the same trend as the changes in the induction period. The *trans*-2-butene/*cis*-2-butene ratio increased whereas the B_1/B_2 ratio and the value of S_2 decreased with an increasing hydrogen content in the reaction feed. These trends emphasize the tendency for *n*-butane formation, as the hydrogen content was increased, while the 1,4-addition of hydrogen to form 2-butenes, in particular the cis isomer, became more pronounced.

2. Characterization Studies. *2.1. Temperature-Programmed Oxidation/Reduction Studies.* With the
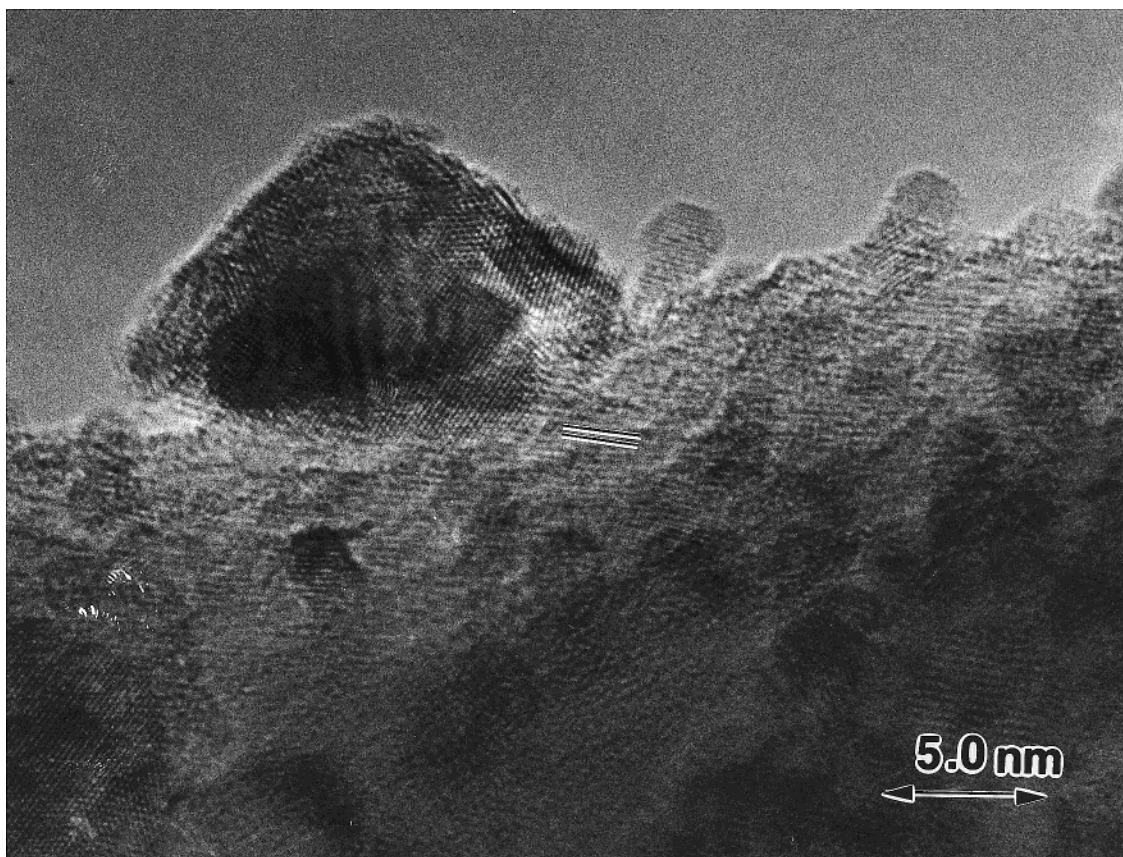
Figure 3. High-resolution transmission electron micrograph showing the appearance of a nickel particle on the edge of a section of a titania support after reaction in 1,3-butadiene at 120 °C for 12 h. The parallel lines highlight the lattice fringes of the support medium.

use of this approach, it is a relatively simple task to ascertain the existence of any changes in weight that take place when a given sample is heated in an oxidizing or reducing environment. In this way, it is possible to pinpoint the conditions where bulk transformations in the chemical nature of a catalyst might be expected. In the current investigation, samples of all the oxide-supported nickel catalysts were heated in both 10% oxygen/helium and 10% hydrogen/helium mixtures at temperatures up to 350 °C. Under these conditions, there were no detectable changes in the weights of the samples indicating that the catalysts maintained their bulk chemical state and were thermally stable up to this temperature.

2.2. XRD Analysis. XRD studies were carried out on both the individual fresh samples and after their extended use in both of the hydrocarbon hydrogenation reactions. Even after careful passivation procedures were followed, it was not possible to ascertain, with any degree of certainty, if any transformations had occurred in the chemical states of the various oxide supports during these reactions.

2.3. Transmission Electron Microscopy Studies. TEM examinations of the supported nickel catalysts showed that the appearance of the metal crystallites did not exhibit any discernible changes in shape after reaction in either 1-butene or 1,3-butadiene. Indeed, it was evident that with the Ni/TiO$_2$ samples, the particles retained their well-faceted morphology, similar to those observed on a corresponding fresh catalyst. One difference was the general increase in particle size after the samples were used in the hydrocarbon hydrogenation

reactions. An example of this condition is presented in Figure 3: a high-resolution electron micrograph, showing the accumulation of nickel particles at the edge of the support, of a specimen that had been exposed to 1,3-butadiene at 120 °C for 12 h.

Close inspection of this micrograph reveals the existence of lattice fringe images of both the metal and support, which provides information on a number of salient points regarding the events that transpired during the reaction. The *d* spacing of the lattice of the metal particle, as measured from the negative of this micrograph, was 0.202 nm, which can be compared with the literature value of 0.203 nm for Ni(111). Perhaps the most interesting features were the values measured for the *d* spacings of the support lattices in close proximity to the nickel, which were found to be 0.332 and 0.304 nm. These values can be compared with those reported for Ti$_4$O$_7$(120) and Ti$_4$O$_7$(122) of 0.338 and 0.302 nm, respectively. On the other hand, when one measured the *d* spacing of the support lattices in a region remote from a metal crystallite, a value of 0.323 nm was found, which is very close to that of TiO$_2$(110) of 0.325 nm.

An analogous condition is shown in Figure 4: an electron micrograph of a Ni/CaTiO$_3$ specimen that had been reacted in 1,3-butadiene at 120 °C for 12 h. Measurement of the *d* spacings from the lattice fringe images of the support material adjacent to the electron-dense nickel particle gave a value of 0.501 nm, which is in good agreement to the value of 0.496 nm for CaTi$_2$O$_4$(020), the partially reduced form of the initial oxide. Unfortunately, in this case, it was not possible
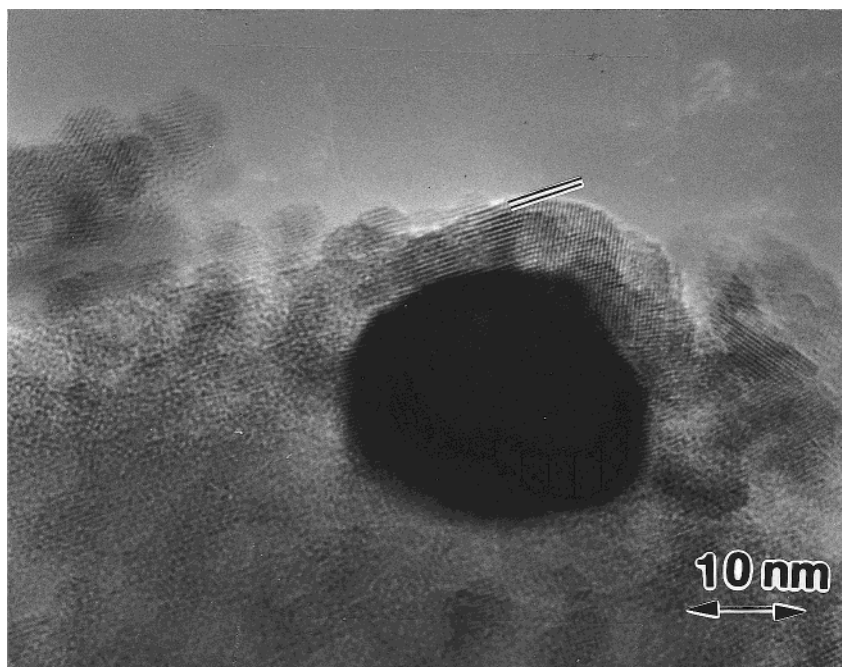
Figure 4. High-resolution transmission electron micrograph showing the appearance of a nickel particle on the edge of a section of a CaTiO₃ support after reaction in 1,3-butadiene at 120 °C for 12 h. The parallel lines highlight the lattice fringes of the support medium.
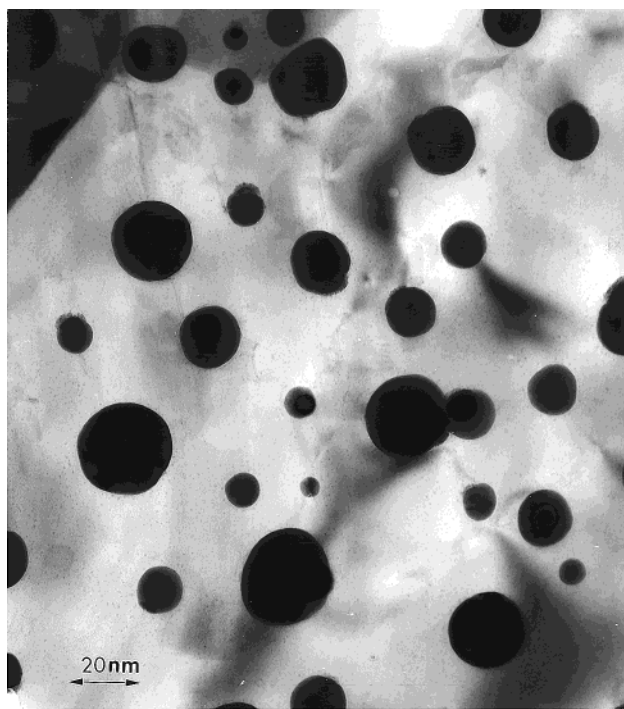

Figure 5. Electron micrograph showing the globular morphology of silver particles supported on titania after heating in 1,3-butadiene at 120 °C for 4 h.

to detect the lattice structure of the support in the regions where metal particles were not present.

The examination of oxide-supported silver specimens that had been subjected to reaction in the hydrocarbon/ hydrogen environments at 120 °C for several hours showed major differences in the morphological characteristics of the metal particles when compared to those displayed by nickel after the same treatments. Figure 5 is an electron micrograph showing the appearance of silver particles supported on titania after reaction in 1,3-

butadiene for 4 h at 120 °C. In this case, the metal particles adopted a globular shape and the average particle size increased by a factor of 3 during the hydrogenation reactions. It was also significant to find that with the Ag/TiO₂ sample, there were no indications for a transformation in the chemical state of the support after exposure to a reducing environment at 120 °C. Consistent with these examinations was the finding from flow reactor studies that the oxide-supported silver systems did not exhibit catalytic activity for either of the hydrocarbon hydrogenation reactions.

Discussion

We have demonstrated that major differences in the catalytic performance of nickel can be achieved, for the hydrogenation of hydrocarbons, by supporting the metal particles on a variety of oxide materials. This aspect was particularly evident when the metal was dispersed on certain dielectric oxides where a dramatic increase in catalytic activity was observed, compared to that obtained with a traditional support medium such as γ-alumina. Furthermore, significant differences were found in the product selectivity patterns exhibited by the various oxide-supported nickel catalysts when these systems were used for the hydrogenation of 1-butene and 1,3-butadiene, respectively.

When one compares the *trans*-2-butene/*cis*-2-butene ratio for both these hydrogenation reactions for a given nickel/oxide support combination, a number of important conclusions can be drawn. It is known that the formation of 2-butenes from the hydrogenation of 1,3-butadiene can occur by two separate reaction pathways: (a) via the isomerization of the partially hydrogenated product 1-butene before its desorption from the catalyst surface or (b) directly as a result of a 1,4 addition of hydrogen to 1,3 butadiene (refs 16–18). While both reaction pathways are equally viable, information leading to the predominant route may be

obtained from a comparison of the *trans*-2-butene/*cis*-2-butene ratios from the hydrogenation of both 1-butene and 1,3-butadiene. If the ratio is similar in both cases, it is then probable that the formation of the 2-butenes occurs via isomerization of 1-butene. On the other hand, if the ratio is significantly different, then the reaction may be assumed to proceed directly from the 1,4 addition of hydrogen to 1,3-butadiene.

Application of this rationale to the current data leads one to conclude that for nickel supported on BaTiO$_3$, TiO$_2$, or γ-Al$_2$O$_3$, it is probable that the formation of 2-butenes occurred primarily via the isomerization of 1-butene, since similar *trans*-2-butene/*cis*-2-butene ratios were attained at 120 °C from the hydrogenation reactions. In contrast, when the metal was dispersed on either Ta$_2$O$_5$ or CaTiO$_3$, significantly different values of this ratio were found for the two reactions giving rise to the belief that on these support materials, the formation of 2-butenes occurred directly from a 1,4 addition of hydrogen to 1,3-butadiene.

The unusual patterns of behavior exhibited by a 5 wt % Ni/CaTiO$_3$ catalyst, toward the hydrogenation of 1-butene and 1,3-butadiene, upon increasing the hydrogen content of the feed are extremely perplexing. If, as discussed later, the catalytic activity and length of the induction period are closely related to the ability of the system to dissociate molecular hydrogen, then one might expect to find similar trends for both of these hydrogenation reactions. As reported in Tables 3 and 6, however, completely opposite trends were observed for this catalyst system. In the hydrogenation of 1-butene, an initial increase in the hydrogen content of the feed resulted in a decrease of the time required to attain maximum activity of the catalyst, but this relationship was reversed at a C$_4$H$_8$/H$_2$ ratio of 0.92. Under the same conditions, for the hydrogenation of 1,3-butadiene, the induction period initially increased before exhibiting a decrease at a C$_4$H$_6$/H$_2$ ratio of 0.79. Since hydrogen is expected to exert a similar influence on the nickel catalyst in both these hydrogenation reactions, other factors must be operative in the reaction mechanism. It is conceivable that the two hydrocarbons exhibit different adsorption characteristics on the metal particles, with 1,3-butadiene being more strongly held than 1-butene. Moreover, it is possible that chemisorption of the C=C species and hydrogen occur on the same metal faces. Under these circumstances, the coadsorption of hydrogen will be a more difficult step in the presence of the diene and as a consequence, generation of atomic hydrogen will be inhibited until a critical C$_4$H$_6$/H$_2$ ratio is reached. Once this condition is achieved, the induction period associated with this reaction will be decreased.

In a previous paper, we established the existence of a direct link between the temperature where a given dielectric oxide exhibited a maximum permittivity and the level at which optimum catalytic activity for hydrogenation of ethylene was realized when nickel was supported on the particular material.[14] In the current investigation, we have extended the use of dielectric-oxide-supported nickel catalysts for hydrocarbon hydrogenation to more complex reactions and during the course of this work several new aspects have emerged pertaining to the key factors surrounding the outstanding performance of these systems.

When ethylene/hydrogen mixtures were passed over the dielectric-oxide-supported nickel catalysts, the reaction took place almost immediately at 120 °C. In contrast, with 1-butene and 1,3-butadiene, extremely long induction periods were required for the CaTiO$_3$- and especially the BaTiO$_3$-supported nickel systems to reach their optimum activity levels. This behavior is consistent with the notion that a slow change in the chemical and/or physical properties of the catalyst takes place during this period. Clearly, while the hydrogenation of a simple molecule such as ethylene is a relatively facile process, the corresponding hydrogenation of 1-butene and 1,3-butadiene requires the establishment of a specific metal−surface-atom arrangement for the reactions to proceed in an efficient manner.

In this regard, it is important to stress that nickel has the ability to dissociate molecular hydrogen and, as such, generate atomic hydrogen species that will readily reduce these support materials to a lower oxide state.[19] It was interesting to find that XRD analysis did not indicate the existence of changes in the bulk state of any of the supports. In another series of experiments, attempts were made to follow the reduction of the supports using XPS; however, we failed to establish the existence of any chemical transformation under the conditions used in this study. On the other hand, high-resolution TEM examination of Ni/TiO$_2$ and Ni/CaTiO$_3$ specimens that had been reacted in a 1,3-butadiene/hydrogen mixture at 120 °C provided some very important information. From the measurement of the *d* spacings, obtained from thin regions of the support adjacent to the metal particles, it was possible to establish the formation of the reduced oxide species, Ti$_4$O$_7$ and CaTi$_2$O$_4$, respectively.

In an attempt to verify this theory, silver, a metal that does not dissociate molecular hydrogen, was supported on CaTiO$_3$ and tested under identical conditions. Examination of these specimens by TEM showed that the support remained in the fully oxidized condition, there being no evidence for changes in structure accompanying the reaction. In contrast to the supported nickel catalysts, the corresponding silver system did not display any activity for either of the hydrocarbon hydrogenation reactions even after a prolonged period of time on stream. The inability of a supported silver catalyst to actively participate in the hydrogenation reaction of either 1-butene or 1,3-butadiene lends credibility to the assumption that the dissociation of molecular hydrogen and subsequent reduction of the support are critical steps in the establishment of an active catalyst.

At this juncture, it is pertinent to recall some of the initial studies performed on the origin of the so-called SMSI effect (strong metal−support interaction). Tauster and co-workers[20,21] discovered that when the group VIII noble metals, supported on oxides from groups IIA−IIB, were heated in hydrogen at temperatures in excess of

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500 °C, the systems exhibited unusual chemisorption properties. They attributed the suppression of H_2 and CO chemisorption capacities to the existence of a SMSI. A number of key issues regarding the SMSI effect emerged from investigations of Baker and co-workers[22-24] who used electron microscopy techniques to examine the structural and chemical changes that occurred when platinum/titania samples were heated in hydrogen from 25 to 800 °C. A dramatic transformation in the structure of the support was found at 500 °C, which from a combination of electron diffraction and lattice fringe spacing measurements revealed that during the reaction, TiO_2 was converted to Ti_4O_7. The finding that this change in structure was not detected in the absence of platinum led to the conclusion that the function of the metal was to provide, via dissociation of H_2, a source of H atoms, which were responsible for reducing the support to a lower oxide. In subsequent studies, it was demonstrated that the origin of the so-called SMSI effect was associated with the migration of reduced titania species onto the surfaces of the metal particles.[25-29] The notion that this phenomenon resulted in complete deactivation of the metal led to the development of a novel method of inhibition of catalytic carbon formation on nickel during interaction with hydrocarbons.[30] Studies conducted with silver, a metal that does not dissociate hydrogen, confirmed the role of the metal in the SMSI interaction, since in this case, there was no reduction in the oxide state of the TiO_2 support.[24] In this context, it was significant to find that in the current investigation, the dielectric-oxide-supported silver samples showed no tendency to catalyze either of the hydrocarbon/hydrogen reactions.

It is tempting to correlate the finding of an induction period with the time required for the various oxide support media to undergo a structural and chemical transformation. The different induction periods observed when nickel was supported on $BaTiO_3$ and $CaTiO_3$ may be attributed to the slight displacement of the barium atom in the perovskite unit cell when compared to the position of calcium in the ABO_3 structure. The slight displacement of this Ba cation is significant as $BaTiO_3$ is known to be ferroelectric in nature, whereas $CaTiO_3$ does not exhibit this property. It is probably this feature that accounts for the difference in reduction characteristics of these two materials.

One can argue that changes in the performance of the dielectric-oxide-supported nickel catalysts is related to the establishment of an electronic interaction between the metal and the reduced support materials and that this phenomenon is responsible for the creation of a unique type of site at the interface between the two components. It should be stressed that the concept of electron transfer between metal crystallites and a support medium has been a source of conjecture for many years, particularly with regard to the unusual behavior associated with the SMSI effect.[31-35] In the current investigation, we have operated with these types of support media at much milder conditions and, as such, have not encountered the deactivation steps experienced by other workers. Indeed, it was evident that transformation of the respective supports was limited to the surface regions immediately in contact with the metal particles. In contrast to the studies performed at high temperatures, which for the most part culminated in catalyst deactivation, we have demonstrated that by operating at less severe conditions, dielectric-oxide-supported nickel particles exhibited superior catalytic activity and selectivity compared to that found when the same metal was dispersed on a traditional oxide carrier.

Conclusions

It would appear that partial reduction of the support, particularly in the vicinity of the dispersed metal phase, is the key to the observed high performance of the nickel/dielectric oxide systems with regard to the hydrogenation of hydrocarbons. In many cases, it is necessary to allow the system to remain on stream for prolonged periods of time to attain the optimum activity. One can rationalize the observed induction periods as being the time required to reduce the support to a level where a critical interaction can ensue with the metal particles. The function of the metal in the establishment of this interaction is to act as a dissociation center for hydrogen, thus providing a source of atomic species for subsequent reduction of the support to a lower oxide state at the interface between the two components. The length of the induction period has been shown to be a function of both the nature of the support material and the hydrogen content in the reactant feed. Finally, it is claimed that electronic perturbations in the nickel crystallites are responsible for the unexpected behavior of the dielectric-oxide-supported metal catalysts and that this process results in the generation of a unique type of site at the interfacial region.

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